A Method for Determining Phenol Quantitatively

by Archie J. Weith

1913

Submitted to the Graduate School of the University of Kansas in partial fulfillment of the requirements for the Degree of Master of Science

THE EFFECT OF TEMPERATURE, ACID CONCENTRATION, AND TIME ON THE BROMINATION OF PHENOL FOR QUANTITATIVE DETERMINATIONS.

by

Archie J. Weith.

Presented to the Faculty

of the

GRADUATE SCHOOL

of the

University of Kansas,

In Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE.

January 15, 1913.

PREFACE.

The problems undertaken in this paper were suggested by Dr. L. V. Redman with whom in part the experimental work has been carried out.

It is the purpose of this research to conduct investigations along two lines:

1. A study of the effects of acid concentration, temperature, and excess bromin during the bromination period on the quantitative estimation of phenol by bromination.

2. An attempt to reduce the cost of a phenol determination by decreasing both the amount of potassium bromide used in making the standard bromide-bromate solution, and also the amount of potassium iodide used to reduce the free bromin present in the solution after the bromination of the phenol.

It is quite obvious number 2 to be of

value must be accomplished without decreasing either the speed or accuracy of the determinations.

TABLE OF CONTENTS.

BIBLIOGRAPHY.

1. Jour. Amer. Chem. Soc.,
Vol. 27, p. 16, (1905)

2. Jour. Soc. Chem. Ind.,
Vol. 30, p. 398, (1911)

3. Jour. Soc. Chem. Ind.,
Vol. 31, p. 208, (1912)

4. Jour. Ind. &. Eng. Chem.,
Vol. 4, p. 655, (1912)

5. Beckurts, Arch. Pharm.,
Vol. 224, 561, (1886)

6. Jour. Soc. Chem. Ind.,
Vol.5, p. 546, (1886)

7. Jour. Ind. & Eng. Chem.,
Vol. 4, p. 656, (1912)

8. Jour. Amer. Chem. Soc.,
Vol. 27, p. 15, (1905)

9. Jour. Amer. Chem. Soc.,
Vol. 27, p. 24, (1905)

10. Chem. News,
Vol. 21, p. 103.

THE EFFECT OF TEMPERATURE, ACID CONCENTRATION, AND TIME ON THE BROMINATION OF PHENOL FOR QUANTITATIVE DETERMINATIONS.

The rapid introduction into commerce of synthetic plastic resistives made from phenol and compounds containing mobile methylenes has made the rapid and accurate determination of phenols of great importance. Although this paper deals only with the simplest of the series, C_6H_5OH, it is hoped that the method herein developed, in its general features, may prove suitable for the determination of the higher homologues.

The fact that seventy-two investigators have contributed research papers on the determination of phenols is indicative of the trouble experienced in making accurate assays of phenol. Previous investigators have worked

upon the theory that the bromination of phenol is a slow rate reaction and requires time for completion. To this end they have employed small volumes of rather concentrated solutions, with considerable excess bromine during the bromination period. The result is a precipitate of tribromphenol, dense and almost granular in structure having often the yellow color of the tribromphenol bromide or containing the separate red specks of tetrabrompheno-quinone. As these products[1] are not completely reduced by hydriodic acid, the determinations often varied by one or more per cent.

A complete bibliography of the earlier work is to be found in Lloyd's paper and references to the more recent investigations are found in the researches of Wilkie.[2]

Recently Rhodes and Redman[3] have shown

1. Jour. Amer. Chem. Soc., Vol. 27,p.16, (1905)
2. Jour. Soc. Chem. Ind., Vol. 30,p.398,(1911)
   " " " " " 31,p.208,(1912)
3. Jour. Ind. & Eng. Chem. Vol. 4; p.655, (1912)

that if the solution of phenol have a phenol concentration approximating N/100 during the bromination period, the precipitate is a light flocculent white mass through which the solution can diffuse easily and as a consequence on thorough shaking the reaction is completed in one minute's time; there is no rapid return of the blue color after titration, such as Koppeschaar mentions as incident at times in his method; and from their numbers as published the results are accurate to two or three parts in a thousand. These authors have shown that Lloyd's hypobromite and the bromide-bromate method (Koppeschaar's solution) are equally rapid, accurate, and satisfactory, underproper conditions of acidity and phenol concentration, in forming the white, flocculent, insoluble tribromphenol. The hypobromite solution is shown to have the disadvantage of being unstable when not carefully sealed or kept in air tight bottles, and as a conseq-

uence requiring restandardization every day. The diluting of the phenol solution has entirely prevented the formation of the yellow tribromphenol bromide or the red tetrabrom-pheno-quinone, which have been noted as sources of error by earlier investigators.[4] Errors from these sources were consequently avoided.

There remains, however, to perfect a method for determining phenol, an investigation into:

(a) The effect of acid concentration during the bromination period.

(b) The length of time required for the liberation of the iodine by the bromine.

(c) The necessary excess of free bromine to be used.

(d) The effects of temperature.

(e) The excess of potassium bromide necessary in the bromide-bromate solution.

4. Beckurts, Arch. Pharm. Vol. 224, p. 561, (1886)

The only equipment required for the investigation was a mechanical shaker,[5] several half-liter ground-stoppered bottles, and standardized burettes.

The solutions used were as follows: N/10 sodium thiosulphate, N/10 bromide-bromate, N/10 phenol, 20% (by Wt.) potassium iodide, hydrochloric acid (S.G. 1.2), and a starch solution made by stirring 5 grams of starch into a liter of water, heating slowly until a clear solution is obtained, and allowing the gelatinous material to settle out.

The thiosulphate solution was prepared by dissolving 125 grams of sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$ in 5 liters of water; 2.76 grams of potassium bromate and 43 grams of potassium bromide per liter of solution constituted the bromide-bromate solution; a later solution in which the potassium bromate was 2.76 grams per liter but the bromide was reduced to 15

5. Jour. Ind. & Eng. Chem., Vol. 4, p. 656, (1912).

grams per liter was found to be quite as satisfactory as the 43 grams per liter. The higher bromide content was introduced in the earlier methods to prevent the formation of tribromphenol bromide,[6] but in the dilute solutions is quite unnecessary, as is shown later in this paper. The phenol solution was made from the third distillate at 181-2° C. of Merck 's c.p. phenol, 1.56 grams being dissolved and made up to one liter.

The 20 % potassium iodide solution was made by dissolveing 200 grams of c.p. KI in 800 cc. of distilled water. The solution was not made up fresh each day as is frequently recommended. A liter of the solution required only a few drops of N/10 thiosulphate to reduce the free iodine which was formed in the solution during three weeks.

The Effect of Acid Concentration.

In each of the following tables the order

6 Lloyd. Jour. Am. Chem. Soc. Vol. 27, p. 15.

from left to right is the order in which the solutions were added for the determinations. The tables in each case show the amount of water added for dilution, the amount of acid added and the resulting normality reckoned for the total volume of the solution after the addition of the bromide-bromate solution, i.e. the acid concentration during the bromination period. The excess bromine calculated and observed are given, and are expressed in percentages of the amount of bromine required to form tribromphenol of all the phenol present in the solution. The length of time given for the bromination, or the "reaction period", is expressed in minutes, as is also the time given to liberate the iodine from the potassium iodide by the excess bromine. The amounts of 20% potassium iodide solution added and the amounts of thiosulphate used for titrating back the free iodine are expressed in cc's and the final solumn gives the percentage of phenol found in each experiment.

T A B L E I.

Acid Concentration.

No. of Ex.	H_2O cc.	HCl Normality cc.	Phenol Sol. cc.	Br. Sol. cc.	% Excess Bromine Cal.	% Excess Bromine Obs.	Reaction period for Br.	KI Sol. cc.	Time to liberate Iodine	$Na_2S_2O_3$ cc.	% phenol found.
1.	50	1 0.16	15.00	15.00	1.6	69.0	1	1	3	10.35	31.47
2.	50	1 0.16	15.00	15.00	1.6	60.5	1	1	3	9.07	40.77
3.	50	1 0.16	15.00	15.00	1.6	14.0	1	1	3	2.07	87.58
4.	50	1 0.16	15.00	15.00	1.6	4.4	1	1	3	0.65	97.21
5.	50	2 0.16	14.97	15.28	3.6	6.5	1	1	3	1.20	97.09
6.	50	2 0.32	14.99	15.27	3.5	5.7	1	1	3	0.87	97.70
7.	50	2 0.32	14.98	15.27	3.5	4.8	1	1	3	0.75	98.37
8.	50	3 0.48	15.00	15.00	1.6	1.4	1	1	3	0.21	100.20
9.	50	3 0.48	15.00	15.00	1.6	1.5	1	1	3	0.22	100.10
10.	50	4 0.64	15.00	15.00	1.6	1.7	1	1	3	0.25	99.91
11.	50	4 0.64	15.00	15.00	1.6	1.7	1	1	3	0.26	99.88
12.	50	5 0.64	24.90	25.00	1.9	1.9	1	1	3	0.49	100.00
13.	50	5 0.64	24.95	25.00	1.7	1.8	1	1	3	0.44	99.97
14.	50	6 0.96	15.00	15.00	1.6	1.5	1	1	3	0.23	100.08
15.	50	6 0.96	15.00	15.00	1.6	1.6	1	1	3	0.23	100.03
16.	50	7 1.12	15.00	15.00	1.6	1.6	1	1	3	0.24	100.00
17.	50	7 1.12	15.00	15.00	1.6	1.7	1	1	3	0.26	99.88

KI Sol. = 20% Thio. = 0.1 N. HCl = S. G. 1.2
Phenol = 0.09843 Br. = 0.1 N. Temp.= 22° C.

The results in Table I (page 14) show very clearly that the solution must have an acid concentration of at least 0.48 N., if the bromination is to be complete in one minute's time. An increase in acidity from 0.48 N. to 1.12 N. does not in any way affect the results. Later Table V will show that the weaker acid solutions are quite satisfactory if speed is not required, in other words if a longer reaction period than one minute be allowed, complete bromination may be effected in acid solutions less than 0.48 N.

As an increase of the acid[7] to 10% does not affect the accuracy of the results by freeing a measurable quantity of iodine from the hydriodic acid during the determination, 0.84 N. acid is recommended as a safety factor for securing rapid and accurate results.

7. Lloyd. Jour. Amer. Chem. Soc. Vol. 27,p.24, (1905)

T A B L E II.

Potassium Iodide-Time.

No. of Ex.	H_2O cc.	HCl cc.	HCl Normality.	Phenol Sol. cc.	Br. Sol. cc.	% Excess Bromine. Cal.	% Excess Bromine. Obs.	Reaction period for Br.	KI Sol. cc.	Time to liberate Iodine.	$Na_2S_2O_3$ cc.	% Phenol found.
18.	50	5	0.80	14.99	15.28	3.5	3.4	1	0.1	1	0.49	100.1
19.	50	5	0.80	14.99	15.28	3.5	3.4	1	0.1	1	0.50	100.1
20.	50	5	0.80	14.99	15.28	3.5	3.7	1	0.1	3	0.55	99.82
21.	50	5	0.80	14.97	15.28	3.7	3.8	1	0.1	3	0.55	99.95
22.	50	5	0.80	14.97	15.28	3.7	3.9	1	0.5	1	0.57	99.80
23.	50	5	0.80	14.98	15.28	3.6	3.8	1	0.5	1	0.56	99.81
24.	50	5	0.80	14.98	15.91	7.9	7.7	1	0.5	3	1.12	100.20
25.	50	5	0.80	14.99	15.91	7.9	7.7	1	0.5	3	1.14	100.12
26.	50	5	0.80	14.99	15.28	3.5	3.4	1	1.0	1	0.53	100.05
27.	50	5	0.80	14.99	15.28	3.5	3.5	1	1.0	1	0.52	100.00
28.	50	5	0.80	14.99	15.28	3.5	3.4	1	1.0	2	0.53	100.05
29.	50	5	0.80	14.99	15.28	3.5	3.4	1	1.0	2	0.53	100.05
30.	50	6	0.80	24.90	25.00	2.0	2.0	1	1.0	3	0.49	100.00
31.	50	6	0.80	24.95	25.00	1.8	1.8	1	1.0	3	0.44	99.97
32.	50	6	0.80	20.00	20.04	1.8	1.8	1	5.0	3	0.35	100.02

KI Sol. = 20% Thio. = 0.1 N. HCl = S. G. 1.2
Phenol = 0.09843 N. Br. Sol. = 0.1 N. Temp. = 22° C.

Table II (page 16) deals with the length of time and the amount of potassium iodide required to reduce the excess free bromine in the solution with the simultaneous freeing of a proportional amount of iodine. In experiments 18, 19, 20, and 20 the amount of 20% potassium iodide solution added was only 0.1 cc. or about 100% more than is required to reduce the excess bromine present. The time given for the potassium iodide to reduce the excess bromine and liberate the iodine was one minute in experiments 18, and 19, and 3 minutes in experiments 20 and 21.

In every case the determination is within 0.2% which is within the limit of error for the reading of the three burettes. Excess of potassium iodide above 0.1 cc. had no effect upon the determination of the free bromine. Three minutes shaking to free the iodine gave results which did not vary from the one minute determinations. This is not in agreement

with Rhodes and Redman's statement that an error of 0.5% may be introduced with only one minutes shaking after the addition of the potassium iodide. As no account was taken of temperature in their experiments (laboratory temperatures), it is very probable that the 1/2% error which they record as due to incompleteness in the freeing of the iodine in one minute may be more properly attributed to incomplete bromination due to low temperatures in the laboratory.

Table III (page 19) records the effect of excess bromine during the bromination period. The experiments show that the phenol present is changed quantitatively into tribromphenol in one minute's time, without any large excess of bromine, if the proper dilution, acidity and temperatures be observed, e.g.- in experiments 33, and 34, 2% excess bromine was used and the reaction was quite complete. Larger amounts of excess bromine

T A B L E III.

Excess Bromine.

No. of Ex.	H_2O cc.	HCl cc.	HCl Normality.	Phenol Sol. cc.	Br. Sol. cc.	% Excess Bromine. Cal.	% Excess Bromine. Obs.	Reaction period for Br.	KI Sol. cc.	Time to liberate Iodine.	$Na_2S_2O_3$ cc.	% Phenol found.
33.	50	6	0.8	24.95	25.00	1.8	1.8	1	0.1	1	0.44	99.97
34.	50	6	0.8	20.00	20.04	1.8	1.8	1	0.1	1	0.35	100.02
35.	50	5	0.8	14.99	15.28	3.5	3.4	1	0.1	1	0.49	100.10
36.	50	5	0.8	14.99	15.28	3.5	3.4	1	0.1	1	0.50	100.10
37.	50	5	0.8	14.98	15.91	7.9	7.7	1	0.5	1	1.12	100.20
38.	50	5	0.8	14.99	15.91	7.9	7.7	1	0.5	1	1.14	100.12
39.	50	5	0.8	14.98	18.29	12.29	12.1	1	0.5	1	1.78	100.10
40.	50	5	0.8	14.99,	19.10	29.5	29.4	1	0.5	1	4.36	100.12

KI Sol. = 20% Thio. = 0.1 N.
Phenol " = 0.09843 N. Br. Sol. = 0.1 N.
HCl = S. G. 1.2 Temp. = 22° C.

(i.e. up to 30%) had no effect upon the determinations. It may be noted, however, in determining unknown solution that the bromide-bromate solution must be added until a slight yellow color, indicating free bromine, remains permanently after shaking. This generally necessitates 5 to 7 per cent excess bromine, if the yellow color is to be seen easily. To one accustomed to the method, 2% excess bromine can be detected. The smaller the amount of bromine in excess the less will be the possible loss from evaporation and such great care is not necessary in preventing the escape of free bromine.

The effect produced upon the determinations by changes of temperature when the bromination period is one minute is shown in Table IV (page 21). ,At 2° C. the bromination is not complete in one minute and no precipitate of tribromphenol is formed. (Later experiments in Table VI will show that

TABLE IV.

Changes of Temperature.

No. of Ex.	H_2O cc.	HCl Normality	Phenol Sol. cc.	Br. Sol. cc.	% Excess Bromine Cal.	% Excess Bromine Obs.	Reaction period for Br.	cc.	Time to liberate Iodin.	cc.	$Na_2S_2O_3$ cc.	Temp. at end of titration.	% Phenol found.
41.	50	5 0.8	14.99	15.25	3.2	12.5	1	1.0	1	1.84		2° C.	90.88
42.	50	5 0.8	15.00	18.46	25.0	37.4	1	5.0	1	5.52		2° C.	87.66
43.	50	5 0.8	15.00	18.46	25.0	27.3	1	5.0	1	4.03		2° C.	97.74
44.	50	5 0.8	14.97	15.28	3.8	16.7	1	1.0	1	2.41		2° C.	87.34
45.	50	5 0.8	14.98	15.28	3.5	3.9	1	0.1	1	0.60		17° C.	99.56
46.	50	5 0.8	14.99	15.28	3.5	4.0	1	0.1	1	0.60		17° C.	99.50
47.	50	5 0.8	14.99	15.28	3.5	3.9	1	0.1	1	0.57		18° C.	99.63
49.	50	5 0.8	14.98	15.28	3.6	4.0	1	0.1	1	0.60		18° C.	99.56
50.	50	5 0.8	14.99	15.28	3.5	3.4	1	0.1	1	0.49		22° C.	100.10
51.	50	5 0.8	14.99	15.28	3.5	3.4	1	0.1	1	0.50		22° C.	100.09
52.	50	5 0.8	14.98	15,26	3.5	3.3	1	0.1	1	0.49		26°C.	100.20
53.	50	5 0.8	14.98	15.26	3.5	3.3	1	0.1	1	0.50		27° C.	100.10
54.	50	5 0.8	14.99	15.28	3.4	3.3	1	0.1	1	0.49		30° C.	100.10
55.	50	5 0.8	14.99	15.28	3.5	3.1	1	0.1	1	0.46		33° C.	100.40
56.	50	5 0.8	14.98	15.28	3.5	3.0	1	0.1	1	0.44		34° C.	100.62
57.	50	5 0.8	14.98	16.55	12.3	11.0	1	1.0	1	1.61		39° C.	101.30
58.	50	5 0.8	14.98	15.28	3.5	1.2	1	0.1	1	0.17		54° C.	102.45

KI Sol. = 20% Thio. = 0.1 N. HCl = S. G. 1.2
Phenol Sol.= 0.09843 N. Br. Sol. = 0.1 N.

at 2° C. complete bromination is effected only after fifteen minutes shaking). At 17° C. and 18° C. the results are still one-half per cent low with the one minute's shaking. For temperatures ranging from 22° C. to 30° C., the results are very satisfactory and accurate. Above 30° C. the amount of phenol determined is too high. This error is due to increased activity of the iodine at the higher temperatures in oxidizing the thiosulphate and tetrathionate to sulphate.[8]

In Table I, it was shown that the concentration of the acid in the solution during bromination must be at least 0.48 N. if the reaction is to be complete in one minute. In Table V (page 23) it is evident that the weaker acid concentrations will effect complete bromination if a longer reaction period be allowed. If the acid concentration is 0.16 N. the reaction requires 15 minutes for complet-

8. Wright. Chem. News, Vol. 21, p. 103.

T A B L E V.

Acid - Time.

No. of Ex.	H_2O cc.	HCl cc.	HCl Normality.	Phenol Sol. cc.	Br. Sol. cc.	% Excess Bromine Cal.	% Excess Bromine Obs.	Reaction period for Br.	KI Sol. cc.	Time to liberate Iodine.	$Na_2S_2O_3$ cc.	% Phenol found.
59.	50	1	0.16	15.00	15.00	1.6	14.0	1.0	1.0	1	2.07	87.54
60.	50	1	0.16	15.00	15.28	3.5	11.1	7.5	1.0	1	1.69	92.45
61.	50	1	0.16	15.00	15.28	3.5	3.7	15.0	1.0	1	0.53	99.83
62.	50	1	0.16	14.98	15.28	3.7	3.7	15.0	1.0	1	0.51	100.03
63.	50	2	0.32	14.99	15.27	3.5	5.7	1.0	1.0	1	0.87	97.70
64.	50	2	0.32	15.00	15.28	3.5	3.7	2.5	1.0	1	0.54	99.84
65.	50	2	0.32	15.00	15.28	3.5	3.5	5.0	1.0	1	0.52	99.97
66.	50	2	0.32	15.00	15.30	3.7	3.4	5.0	1.0	1	0.50	100.23

KI Sol. = 20% Thio. = 0.1 N.
Phenol Sol. = 0.09843 Br. Sol. = 0.1 N.
HCl = S.G. 1.2 Temp. = 22° C.

ion, while the reaction is complete in 5 minutes if the acid concentration be increased to 0.32 N.

The experiments recorded in Table VI (page 25) indicate that the bromination of the phenol is not complete in 0.8 N. acid in one minute's time if the solution is kept at 2° C. Fifteen minute's shaking is required at this low temperature to complete the reaction. In these low temperature experiments a precipitation of the tribromphenol did not begin until the solution had been shaken for three minutes.

Tables V and VI show that the two principal factors in completing the bromination of the phenol in one minute's time are acid concentration and temperature. The temperature should be roughly 20 - 30 ° C., and the acid concentration 0.5 N. to 1.0N.

T A B L E VI.

Reaction Period
With Strong Acid at Low Temperatures.

No. of Ex.	H_2O cc.	HCl cc.	HCl Normality.	Phenol Sol. cc.	Br. Sol. cc.	% Excess Bromine. Cal.	% Excess Bromine. Obs.	Reaction period for Br.	KI Sol. cc.	Time to liberate Iodine.	$Na_2S_2O_3$ cc.	Temp. end of titration.	% phenol found.
67.	50	5	0.8	14.99	15.28	3.3	12.5	1	1.0	1	1.84	2° C.	90.88
68.	50	5	0.8	15.00	15.28	3.5	5.3	5	1.0	1	1.00	2° C.	98.27
69.	50	5	0.8	15.00	15.28	3.5	4.1	10	1.0	1	0.60	2° C.	99.41
70.	50	5	0.8	15.00	15.28	3.5	3.4	15	1.0	1	0.50	2° C.	100.10

KI Sol. = 20%
Phenol Sol. = 0.09843 N.
HCl = S.G. 1.2

Thio. = 0.1 N.
Br. Sol. = 0.1 N.

EXCESS BROMIDE
in Bromide-Bromate Solution.

A standard bromide-bromate solution, (Koppeschaar's solution) consists of 2.76 grams of potassium bromate and 43.1 grams of potassium bromide per liter. According to the reaction;

$$KBrO_3 + 5KBr + 6HCl = 6KCl + 3Br_2 + 3H_2O$$

2.76 grams of potassium bromate requires 9.8 grams of potassium bromide, consequently the amounts stated above give an excess of 340 per cent of bromide.

Such a large excess of potassium bromide seemed to the author unnecessary in this method although it has been pointed out by S. J. Lloyd[9] that the rate of formation of tribromphenol bromide is decreased by the addition of potassium bromide. A bromide-bromate solution was,

9. Jour. Am. Chem. Soc. Vol. 27, p.15, (1905)

therefore, made up containing 2.76 grams of potassium bromate and 15 grams of potassium bromide per liter, giving an excess of 50 per cent of potassium bromide over that required by the above equation.

The results recorded in Table VII (page 28) show that a decrease of 290 per cent in the excess potassium bromide does not affect the accuracy of determinations by this method. The tribromphenol precipitate was of the same flocculent nature as that from the bromide-bromate solution with the higher potassium bromide content, and in no instance was there a yellowish tinge, indicative of tribromphenol bromide, in the white precipitate. The results in the table show that if any tribromphenol bromide was formed it was quantitatively reduced by the free hydriodic acid.[10]

10. Lloyd. Jour. Am. Chem. Soc. Vol. 27, p. 15, (1905)

T A B L E VII.

Excess Bromide in the Bromide-Bromate Solution.

No. of Ex.	H_2O cc.	HCl cc.	HCl Normality.	Phenol Sol. cc.	Br. Sol. cc.	% Excess Bromine. Cal.	% Excess Bromine. Obs.	Reaction period for Br.	KI Sol. cc.	Time to liberate Iodine.	$Na_2S_2O_3$ cc.	% Phenol found.
71.	50	5	0.8	15.00	15.20	3	3	1	0.1	1	0.42	100.1
72.	50	5	0.8	15.00	15.20	3	3	1	0.1	1	0.44	99.9
73.	50	5	0.8	14.99	15.19	3	3	1	0.1	1	0.44	99.9
74.	50	5	0.8	15.00	16.47	12	12	1	0.1	1	1.67	100.1
75.	50	5	0.8	15.98	17.74	12.7	12.7	1	0.1	1	1.99	100.1

KI Sol. = 20%
Phenol Sol. = 0.09843 N.
HCl = S. G. 1.2

Thio. = 0.1 N.
Br. Sol. = 0.1 N.
Temp. = 22° C.

It may be mentioned that if one overshoots with the thiosulphate back titration by the use of the bromide-bromate solution, directly, should not be practiced. The free bromine oxidizes the thiosulphate and tetrathionate to sulphate and errors amounting to 22% of the quantity of the bromide-bromate solution used for back titration may be introduced.

To avoid the necessity of a standard iodine solution for back titration, we have used the following method and have found it both accurate and convenient. To 10cc. of water in a test tube, add 1 cc. strong hydrochloric acid, 4 or 5 drops of bromide-bromate solution, carefully measured from the burette, a few drops of 20% solution of potassium iodide, and as soon as the iodine is liberated, wash the liquid from the test tube into the determination bottle. If a sufficient quantity of the bromide-bromate solution has

been taken the blue starch iodide color is at once restored, and titration with the thiosulphate can be continued to an accurate end point.

DIRECTIONS.

(1) Solutions required are 0.1 N. sodium thiosulphate (24.8 grams per liter); 0.1 N. Bromide-bromate (2.76 grams $KBrO_3$ and 15 grams KBr per liter); 20% potassium iodide and 0.5% starch solution. The bromide-bromate solution must be compared with the sodium thiosulphate by adding acid and potassium iodide and titrating the iodine set free.

(2) Into a 500 cc. bottle fitted with a ground glass stopper, put 50 cc. water, 5 cc. hydrochloric acid (S.G. 1.2), and then add 15 cc. of the unknown phenol solution which is to be determined and which has been diluted to approximately 0.1 N. If the solution is weaker than 0.1 N., no previous dilution is necessary.

Add, while shaking slowly, enough 0.1 N. bromide-bromate solution to give the solution

in the bottle a slight yellow color which remains permanently. The temperature of the liquid at this point should be about 22° C. Place the stopper in the bottle, giving it a sharp twist to bring the surfaces firmly together, and shake continuously for one minute.

Remove the stopper, add to the solution in the bottle 0.5 cc. potassium iodide solution (20%), replace the stopper and again shake continuously for one minute. Wash down the stopper and sides of the bottle and titrate the solution with 0.1 N. sodium thiosulphate, using starch solution as indicator. The starch solution should not be added until enough sodium thiosulphate has been run in to make the solution almost colorless. It is well, before the blue color of the starch iodide has entirely disappeared, to replace the stopper and shake the bottle vigorously. Care should be taken not to over-shoot the end point and a standard tribromphenol with excess

of sodium thiosulphate should be at hand for comparison. As a further precaution the solution may be left a faint blue as less error is introduced in this way than by titrating to colorless with the attendant danger of overshooting. In case of overstepping the end point, a solution containing free iodine should be used for titrating back. If a solution containing or yielding free bromine be used for back titrating concordant results are not obtained.

The difference between the quantity of sodium thiosulphate used and the known quantity of bromide-bromate solution added, gives the amount of bromide-bromate solution used up by the phenol solution in the formation of tribromphenol. Each cubic centimeter of 0.1 N. bromide-bromate solution is equivalent to 0.0015675 grams phenol.

SUMMARY.

1. The results show that phenol may be determined rapidly by bromination with a maximum possible error of 0.00005 grams.

2. The quantities of reagents for determining phenol as generally recommended have been decreased without sacrificing either speed or accuracy.

(a) 2% excess of free bromine is sufficient for the complete bromination of phenol in one minute in an acid solution of 0.8 N. at 22° C.

(b) A large excess (over 50%) of potassium iodide above that necessary for complete reduction of the free bromine according to their equation is not required.

(c) It has been shown that not more than 50% excess potassium bromide over that

called for by the equation (See page 26) need be used in making the standard bromide-bromate solution. The U. S. P. calls for an excess of 340%.

3. Complete liberation of the iodine by the free bromine may be effected in one minute, if thorough diffusion be obtained by sufficient shaking.

4. The acidity of the solution in which the tribromphenol is precipitated must not fall below 0.48 N. if the bromination is to be complete in one minute. An acidity of 0.5 N. to 1.0 N. is recommended.

5. Low temperatures have a retarding influence on the rapid formation of tribrom-. phenol. Temperatures between 20 ° C and 30° C. are recommended.